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THE STRUCTURE OF INORGANIC SOIL

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THE STRUCTURE OF INDRGANIC SCIL

RY

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> Cambridge, Massachusetts October, 1953

FIGURE LIST

Number	Title		
1	Nonpolar System		
2	Dipole		
3	Water Molecule		
4	The Orientation Effect		
5	The Hydrogen Bond		
6	Kaolinite		
7	Pyrophyllite		
8	Kaolinite		
9	Colloid Double Layer		
10	Potential Between Two Colloids		
11	Attractive and Repulsive Potential		
12	Total Potential Energy Between Two Colloids		
13	Effect of Electrolyte Concentration on Potential Energy		
1/4	Soil Water		
15	Adsorbed Water		
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I. INTRODUCTION

Soil has been used for an engineering material for many centuries; in fact, some ten thousand years ago Neolithic man employed earth and stone to make his tombs. Frior to the birth of soil mechanics in the early part of the Twentieth Century, soil engineering was essentially an empirical art. Soil mechanics changed soil engineering to an applied science in which fundamental laws were employed to compute numerical answers.

Soil mechanics sparked an extremely rapid growth in soil engineering. One can now rightly wonder, however, if the frame-work of soil mechanis is broad, strong and sound enough to support its continued healthy growth. Does this framework of facts, theories, and analogies so ingeniously and quickly constructed need critical examination and strengthening?

The author's opinion that such strengthening is necessary prompted the preparation of this paper by an engineer for engineers. It attempts to give a detailed and consistent picture of the structure of inorganic cohesive soil. This picture, while more complicated than those prevalent in soil engineering today, is felt to be the start of what must be ultimately developed if phenomena such as soil strength are to be adequately understood. The control or alteration of soil properties is predicated on an understanding of soil structure.

The most important consideration of soil structure is the nature and magnitude of forces between the soil particles and between soil and water. The possible linkages between the various parts of matter are described first. The basic unit, the soil crystal, and the soil aggregate are progressively built up from atoms, employing the previously described linkages and the principles of colloidal chemistry. The resulting concept of soil structure is subjected to examination in the light of experimental

^{*}There have been a number of structural theories advanced (Terzagii, 1925, 1941, Casagrande, 1932, Winterkern and Tschebotarioff, 1947, Grim, 1942, Russell, 1932, etc.). Several of these theories are significant contributions to the literature on soils. The present day inadequacies of the various theories lie more in their generality and incompleteness than in erroneous concepts.

data and is used to explain many of the scil phenomena anown to the scil engineer.

This structural theory is not advanced as a complete and final treatise, but is intended as a working hypothesis to be expanded as theory and experimental data become available. It should initiate and guide research on this vital subject.

II. BONDS AND LINKAGES

Atoms can bond (intramclecular bonds) to other atoms to form molecules; atoms in one molecule can also bond (intermolecular bonds) to atoms in another molecule. There are five types of intramolecular bonds, which are called primary valence bonds. The two intermolecular forces, called secondary valence forces, are van der Waals and hydrogen bonds.

III. PRIMARY VALENCE BONDS*

The primary valence bonds are: the <u>covalent bond</u>, the <u>heter-polar bond</u>, the <u>ionic bond</u>, the <u>coordinate bond</u> and the <u>metallic bond</u>. Since the transition from one type of bond to another can be gradual, the classification of certain forces is arbitrary.

An explanation of these bonds, which is satisfactory for elementary work, can be made in terms of atoms completing their outer electron shells.

Since the primary valence bonds in cohesive soils are seldom broken, they are of minor concern to the engineer. Certain of these bonds, expecially the heterpolar and the ionic, result in nonsymmetrical configurations and, therefore, are the source of residual electrical charges. These charges are of concern to the engineer and are discussed later.

IV. SECONDARY VALENCE FORCES (also called residual valence forces, van der Waals forces, van der Waals-London forces, intermolecular forces of attraction, and intermolecular cohesive forces.)

Secondary valence forces acting between molecules are attributed to the presence of electric moments in the individual molecules.

^{*} For a detailed treatment of bonds see The Nature of the Chemical Bond, by Linus Pauling, Cornell University Press, 1948, and Crystal Chemistry, by R. C. Evans, Cambridge University Press, 1948.

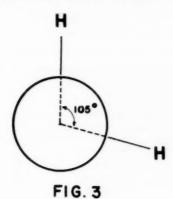
If, in an electrical system, the center of action of the positive charges coincides with the center of action of the negative charges, the system has no dipole moment, For example, the system in Fig. 1 has no dipole moment, and is termed nonpolar. On the other hand, the system in Fig. 2 has a dipole moment of e. A and is, therefore, polar.

The atoms in the water molecule are held together by a heterpolar bond and the resulting molecule is not electrically symmetrical. Fig. 3 shows that the hydrogen-oxygen bonds are at an angle of 105°, not 180°. The water molecule is therefore a dipole.

FIG. I

WATER MOLECULE

FIG. 2



There are three effects contributing to secondary valence forces, namely:

1. The Orientation Effect

The orientation effect consists of an attraction between the oppositely charged ends of permanent dipoles. Fig. 4 illustrates the orientation effect:

Since thermal agitation tends to upset the alignment of the dipoles, the orientation effect is highly dependent on temperature.

THE ORIENTATION EFFECT

FIG. 4

2. The Induction Effect

Many normally nonpolar molecules become polar when placed in an electric field, since it causes a slight displacement of the electrons and nuclei. Since the movement is induced, the phenomena is called the <u>induction effect</u>; the extent to which it occurs in a molecule is called the <u>polarizability</u> of the molecule. The induction effect is only slightly affected by temperature.

3. The Dispersion Effect

Since all electrons vibrate constantly, there occur in all molecules relative displacements between the electrons and nuclei. These displacements result in temporary dipoles that make intermolecular attractive forces possible. This attractive force, called the dispersion effect, occurs in all molecules and is independent, within the normal temperature ranges, of temperature.

^{*} An indication of the relative contribution of each of the three effects to secondary valence forces can be obtained from the percentage breakdown of energy in the van der Waals forces effective between water molecules, namely:

orientation	77%
dispersion	19%
induction	48

Since the secondary valence forces are so important for an understanding of soil structure, they are considered further in Section X_\bullet

V. THE HYDROGEN BOND

The hydrogen bond is normally considered a secondary valence bond. It is, however, stronger than the usual secondary valence bond, and is somewhat similar in character to the coordinate bond, a primary valence bond. It can be considered a strong secondary or a weak primary valence bond, or a unique bond between the secondary and primary bonds.

The hydrogen bond occurs when an atom of hydrogen is rather strongly attracted by two other atoms. The hydrogen cannot decide to which atom to bond, and oscillates between them. The best example of the hydrogen bond is the bond between water molecules, as shown:

The hydrogen atoms is bonding the water molecules together by its attraction to both. It cannot decide with which oxygen it

wants to share its electron. The hydrogen bond is somewhat similar to a dipolar attraction. Fig. 5 shows that the water molecules line up as .

VI. BOND STRENGTH

An indication of the relative strength of the various bonds and the distance between bonded atoms can be obtained from the typical values given below:

Type of Bond	Strength in Kcal per g-mole	Interatomic or Intermolecular Distance in A°	
Primary valence	20-200	1-2	
Hydrogen	5-10	2-3	
Secondary valence	0.5-5	to >5	

The variation of attractive force, F, between atoms or molecules

as a function of the distance, r, between them is given for various combinations:

1. Ion - ion:
$$F = f(\frac{1}{r^2})$$

2. Ion - dipole:
$$F = f(\frac{1}{3})$$

3. Ion - neutral symmetrical molecule:
$$F = f(\frac{1}{r})$$

4. Permanent dipole-symmetrical molecule:
$$F=f(\frac{1}{r})$$

5. Statistical dipoles:
$$F = f(\frac{1}{r})$$

VII. THE SOIL PARTICLE

There are several terms which will be employed to describe the structure of soil. These terms are defined now and are elaborated on in the following pages.

The <u>sheet</u> or <u>platelet</u> or <u>sandwich</u> is the largest repeating structural array of atoms. The <u>crystal</u> is the largest non-repeating unit and is built up of sheets. The <u>aggregate</u> is a haphazard agglomerate of crystals. The soil <u>particle</u> is the smallest apparent unit of the soil; a particle can be a sheet, a crystal or an aggregate.

VIII. THE SHEET

The minerals which occur in soil include nearly all of those known. While several groups of minerals - oxides, carbonates, silicates, etc., are very common in soil, the silicates are by far the most widespread and abundant. Because of their overwhelming abundance and importance, the silicates will be employed in the following description of soil structure. Further, the clay minerals will be the silicates selected. One should not infer that phenomena like cohesion and plasticity can only be explained for soils containing clay minerals. While it is true that most of the soils exhibiting these properties contain clay minerals, there

^{*} For a detailed treatment of clay mineralogy see X-Ray Identification and Crystal Structures of Clay Minerals, Edited by G. W. Brindley, The Mineralogical Society, London, 1951; "Minerals of the Montmorillonite Group," by C. S. Ross and S. B. Hendricks, Prof. Paper 205-B, U.S. Dept. of the Interior, and Reference Clay Minerals, Research Project 49, American Petroleum Institute, New York, 1949.

are soils which have these properties but contain no clav minerals. In other words, the structures of common minerals are used in presenting the following theory: the types of forces involved exist with other minerals.

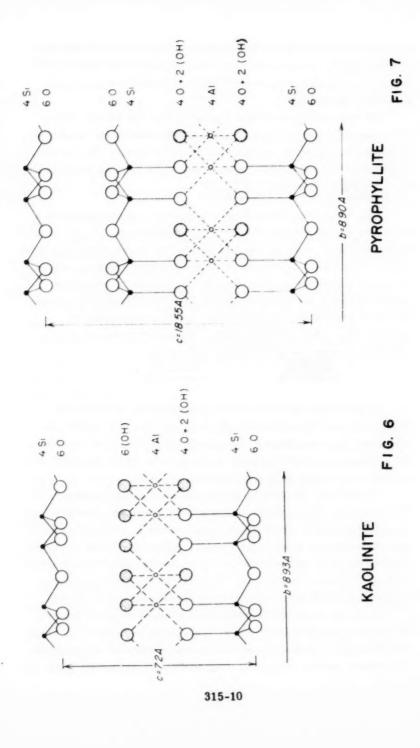
The three most common clay mineral groups are kaolin, illite and montmorillonoid. Fig. 6 (Gruner, 1932) presents the structure of kaolinite, the most common of the kaolin minerals. Kaolinite is a sandwich of silica and gibbsite speets, and can be represented as

Fig. 7 (Pauling, 1930) shows a pyrophyllite sheet which has a structure similar to both illite and montmorillonoid. In the mineral montmorillonite, which is the most common one of the montmorillonoid group, there is a substitution of magnesium for every sixth aluminum in the gibbsite sheet. This substitution results in a negative charge for every six gibbsite cations, cr 1/3 of a negative charge for every two cations, as is apparent in the montmorillonite formula, (Al_{1.67}Mg_{0.33}) Si₁₀10(OH)₂. Montmorillonite can be represented as

In the illite minerals, there is replacement of about 15% of the silicons with aluminums, which causes the illite sheet to have a net negative charge. This charge is partially balanced by non-exchangeable potassium ions, as is pointed out in the next section, and partially by exchangeable cations.

The atoms in the mineral sheets are connected by primary valence bonds. The cation-linkages in the sheets are partially ionic and partially covalent, and are, therefore, considered by some as heterpolar bonds. The crystallographer considers the clay minerals to have ionic structures, since the intrasheet bonds behave effectively as ionic ones. Ionic bonds result in polar configurations; therefore, the sheets possess electrostatic charges.

While the atoms in the basic units of other minerals may be connected by other types of bonds, e.g., graphite by metallic bonds, the interatomic connections within the basic units of all minerals are primary valence bonds. In other words, the intrasheet bonds are



very strong forces and are not likely to be broken by forces which the soil engineer normally applies to soil.

IX. THE MINERAL CRYSTAL

A crystal can vary from a single sheet to hundreds of sheets. The number of sheets in a crystal depends on (among other things, such as the environment during growth) the attractive forces between them and on lattice distortions resulting from isomorphous substitution. The expanding minerals, like montmorillonite, have weak intersheet linkages and considerable isomorphous substitution, and, therefore, often exist as single-sheet crystals when dispersed in water. On the other hand, there have been no reports of single-sheet crystals of kaclinite, which has strong intersheet linkages and little, if any, substitution.

A. Kaolinite

A kaolinite crystal consists of sheets stacked up in such a way that the oxygens of a silicalie on the hydroxyls of a gibbsite. The kaolinite crystal can be represented as Fig. 6 is not to scale and is misleading as to the spacing in a kaolinite crystal. Steric computations show that the clear distance between the top hydroxyls of one sheet and the bottom oxygens of the overlying sheet is 0.16 Å.

The linkage between adjacent sheets in a kaolinite crystal is probably hydrogen bonding. The 0.16 Å between the sheets is short enough for hydrogen bonding to be effective. In addition to hydrogen bonding, there are secondary valence linkages resulting from attraction between polar units (orientation type) and from the dispersion effect.

Fig. 8 is an electrophotomicrograph of a typical kaolinite crystal. It is about lain diameter and 0.08 thick; it, therefore, contains about 115 sheets.

B. Illite

The sheets in an illite crystal are primarily linked together by potassium ions which are an integral part of the illite structure. The connecting potassium in illite plays the same role that the potassium does in the mica, muscovite. The hexagonal holes

^{*} Taken by C. E. Hall of Massachusetts Institute of Technology.

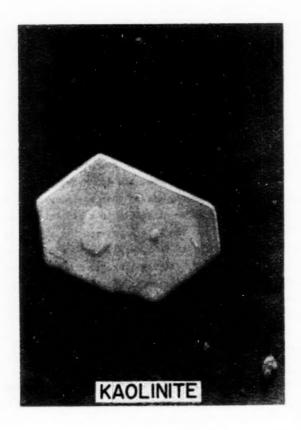


FIG. 8

in the silica sheets are large enough for the potassium ions to fit between sheets and not cause lattice distortion, even if the sheets were touching. The small clear spacing between sheets (0.76 Å) indicates that the potassium ions (radius 1.33 Å) do rest partially within the adjacent sheets; the illite crystal can be

represented as

Aiding the potassium intersheet linkages are secondary valence forces between the sheets. The potassium ions help satisfy the charge de-

ficiency described previously and are, therefore, held to illite sheets by ionic forces. Since the sheets have less symmetry (because of the isomorphous substitution) the orientation effect in illite is weaker than in kaolinite.

C. Montmorillonite

As in illite, the sheets of montmorillonite are thought to be stacked with oxygens of one sheet against those of the adjacent sheet. There can therefore, be no hydrogen bonding between sheets as exists in kaolinite. The isomorphous substitution in montmorillonite is about half of that in illite; this charge is balanced by exchangeable cations between the sheets. Since the net charge density in montmorillonite is considerably less than that in illite, the sheet linkage by cations is considerably weaker than in illite. The clear spacing between sheets in montmorillonite is 0.36 A, so the exchangeable ions must partially fit into the lattice. Montmorillonite can be represented as The montmorillonite intersheet linkage is through the exchangeable cations, aided by secondary valence forces between polar units. Since this linkage is relatively weak, montmorillonite will often disperse into sheets in water.

The following table helps summarize the preceding:

Clay Crystal	Type of Intersheet Linkage	Strength of Linkage
Kaolinite Illite	H-bonding + Secondary Valence K-linkage + Secondary Valence	strong
Montmorillonite	Cation linkage + Secondary Valence	weak

In all soil crystals the bonds between the atoms in the sheets

are too strong to be broken by any normal stress the engineer places on the soil. In only the expanding clays (montmor: llonoids) is the linkage between sheets weak enough to concern the soils engineer.

X. SOIL PARTICLES AS COLLOIDS"

A. Introduction

The consideration of dilute soil-water systems from the viewpoint of classical colloidal chemistry is very helpful to the study of soil structure, since sedimentary clays form from suspensions and since the forces involved in these suspension are present in any in situ clay. We will consider, then, the electrical forces between colloids and the conditions of stability of a colloidal suspension.

3. Soil Colleid

A colloid is a particle whose specific surface (surface area per mass or volume) is so nigh that its behavior is controlled by surface energy rather than mass energy. The smaller any given snaped particle, the larger the surface area per volume. For example, area of a cube whose side dimension is 2 is equal to 6 2 volume $-\frac{6}{7}$; the specific surface of the cube varies, therefore, inversely with its side. A cube lyon a side has an area equal to volume 6 4 .

Clay particles are usually plate, needle or rod shaped; these shapes have higher specific surfaces than a cube of equal volume. For example, the kaolinite particle shown in Fig. 8 has a specific surface (25) about twice that of a cube (13) whose volume is equal to that of the particle. A montmorillonite platelet 0.1 by .002 has a surface area equal to 1000 1, which is five times that volume

of an equivolume cube.

^{*} For a detailed treatment of lyophobic colloids see: Theory of the Stability of Lyophobic Colloids, by Verwey and Overbeek, Elsevier Fublishing Co., 1948, and Colloid Science, Vol. I, Ed. by Kruyt, Elsevier Fublishing Co., 1949. Much of Section X is summarized from these two books..

The above examples show that clay particles have high specific surface because of their size and shape. The upper size limit of a colloid has arbitrarily been set at approximately .2 to l.w..

Nearly all clay particles are colloidal even though the maximum particle dimension of several of the clay minerals - kaolinite, dickite, attapulgite, etc. - is greater than l.w.

C. Source of Potential and Colloid Repulsion

It has been inferred from extensive experimental data that a dispersed colloid carries an electric charge. This charge is caused by an excess of one type of ion in the colloidal structure. For example, a silver iodide, AgI, crystal can have an excess of either Ag⁺ ions or I⁻ ions; in the first case it will carry a net plus charge and in the second a negative charge.

Experiments have shown that nearly always a soil colloid suspended in water carries a net negative charge. This negative charge is easily explained in montmorillonite, where the isomorphous substitution of a magnesium for every sixth aluminum results in one negative charge per substitution. While isomorphous substitution occurs in the other montmorillonoids and in the illites, none has been reported in the kaolins. Excess oxygen ions on the ends and lateral surfaces and local discontinuities, as discussed later in this paper, can cause residual charges in all soil minerals. The acidic nature of soil minerals suggests that hydrogen atoms of the hydroxyl groups come off in the presence of water and thereby give the minerals a net negative charge.

Since the net electrical charge of the entire soil-water suspension must be zero, the charge on each colloid must be neutralized by ions from the water which swarm around each soil colloid. These ions are called "counterions" or "exchangeable ions". The reduction of the particle potential ψ_0 with distance is illustrated in Fig. 9. The counterions would all swarm to the surface of the particle to neutralize the surface charge of the particle, were it not for the thermal activity they possess, and for the attraction exerted on them by other ions and colloids. Their positions are compromises between the particle charge which pulls them in and their thermal activities plus the attraction by other bodies, which keeps them away. The counterions constitute the "diffuse double layer" of

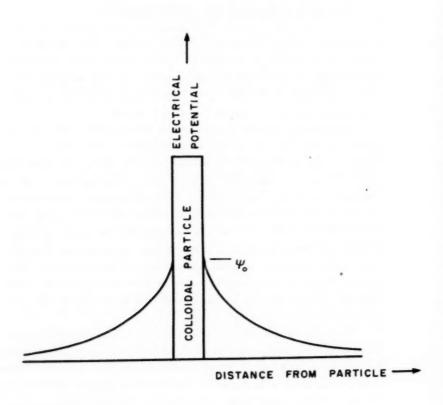


FIG. 9

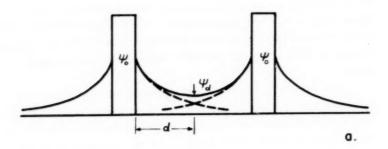
the colloid; the surface charge of the colloid is the other layer of the double layer.

The curve of potential, Ψ versus distance, x, is an exponential one, $\Psi \sim e^{-x}$, and depends on a number of variables in the system. The two most important variables are the valence and the concentration of the ions. The potential varies inversely with the ion valence; for example, for bivalent ions Ψ decreases twice as rapidly with x as for monovalent ions. The potential varies inversely with the square root of the ion concentration; for example, a 10-fold increase in ion concentration would move the $\Psi(x)$ curve toward the carticle surface by 10; i.e., the same Ψ is reached at distances $\frac{1}{10}$ as large.

When two colloids in a suspension approach each other they will reach an interparticle distance where their double layers interact. In Fig. 10 are shown two colloidal plates brought close enough for interaction of their double layers. If the interaction is small (Fig. 10a), the electrical potential due to one double layer will be negligible at the surface of the second plate, and inversely. For this condition, the potential midway between the plates, Ψ_d , will be approximately the sum of the potentials in each double layer. For a given surface potential, Ψ_d decreases exponentially with increasing spacing.

When the colloids come so close together that the electric potential between them is everywhere large, there is strong interaction (Fig. 10b). The potential midway between the colloids is then less than the sum of the potential in each double layer. The most important result of interaction between double layers is the decrease effected in the charge of each double layer. A decrease in charge results in an increase of the free energy of the double layer. Since systems tend to exist in a state of minimum free energy, the colloids repulse each other when their double layers interact. Based on free energy considerations, expressions of repulsive energy between colloids as a function of interparticle distance have been developed.

The influence of ion valence and concentration on the repulsive energy between two colloids is complicated. An increase in ion valence or ion concentration causes a decrease in repulsion for all but small



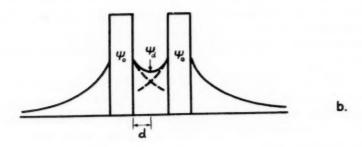


FIG. 10

intercolloidal distances (a few angstroms), where the reverse is true.

D. Colloid Attraction

In the preceding section we considered the diffuse double layer of colloids and the repulsion between colloids resulting from interaction of the double layers. We will now consider the long-range attractive forces which exist between colloids in suspension.

The attractive forces acting between colloids which are far apart are "van der Waals forces" or "van der Waals-London forces". They are electrical in nature, as was explained in Section IV. Debye showed that two dipolar molecules would mutually influence their spatial orientations in such a way that on the average, attraction will occur. As pointed out in Section IV, all molecules are polar in behavior, either permanent dipoles or induced ones. The van der Waals-London forces are, therefore, universal forces acting among all atoms. The force between two atoms varies inversely as seventh power of the distances between them (see Section IV). It has been shown that in an assembly of atoms, the attractive force of one atom for all other atoms is almost independent of the surrounding atoms. In other words, the attractive forces are essentially additive.

The attractive potential between two particles has been worked out by summing up the attractive potentials for all atomic pairs formed by two atoms belonging to different particles. Equations which have been developed for various shaped particles show that the attractive potential between particles dissipates more slowly with increasing interparticle distance than does the attractive potential between two atoms with increasing interatomic distance. The attractive potential for two plates varies inversely as the square of the distance between them.

E. Total Potential Energy Between Two Particles

In the two preceding sections we have considered separately the repulsive and the attractive energies between particles as a function of the distance between them. We now want to consider the total - repulsive plus attractive - energy between two particles.

^{*} The forces were postulated by van der Waals and explained by London on the basis of wave mechanics.

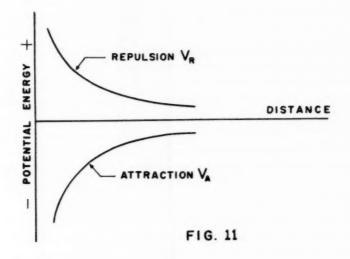
In Fig. 11 are plotted the repulsive, attractive and total energy as a function of the distance between the particles. The repulsive potential, V_R , decreases with increasing distance at more or less an exponential rate. The attractive potential, V_A , decreases in magnitude as the square of the distance. V_A will always be larger than V_R for very small and for very large interparticle distances, since V_A approaches $\mathcal O$ as the distance decreases, while V_R approaches a finite value, since an exponential function approaches zero more rapidly with increasing distance than does a function decreasing with a negative power.

In Fig. 12 are plotted two possible total potential curves. Curve a shows that as the particles approach, the potential energy of the system decreases, i.e., there is attraction between the particles, since the force between the plates is the negative derivative of the potential. The two particles will, therefore, approach each other until they touch and stick, or flocculate.

Curve b, Fig. 12 shows that an increase of energy, or repulsion, results when the particles approach each other. As thermal energy brings the particles toward each other, they will repulse and stay in suspension. If, however, the particles are forced close enough together to pass the hump in the curve, they will come still closer and flocculate, since, to the left of the hump, a decrease in distance results in a decrease in energy.

Since the theory of soil structure presented later involves the effect of a change in ion concentration on the forces between particles, it is well to consider this effect now. In Fig. 13[#] are plotted total energy curves versus half the distance between plates; the different curves are for different ion concentrations, 10⁻⁵ to 10⁻¹ molar for curves 1 to 6 respectively. Fig. 13 illustrates two facts already pointed out: an increase in ion concentration depresses the double layer; the attractive force is always larger than the repulsive force at very small distances.

^{*} Fig. 13 was obtained from Fig. 29 of Verwey and Overbeek (1948) by inserting what are thought to be reasonable soil properties (e.g., \(\psi = 100\) millivolts) in their theoretically calculated curves. The curves are based on an electrolyte of monovalent cation and monovalent anion. The values shown in Fig. 13 are, at least, of the correct order of magnitude.



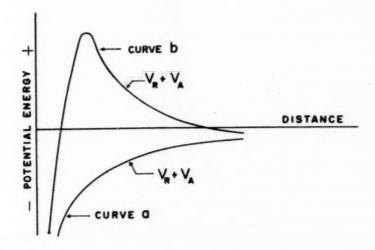
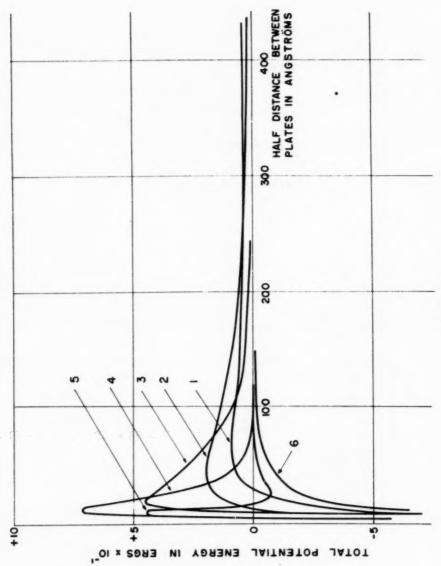


FIG. 12



315-22

Fig. 13 shows that a slight increase in electrolyte content of a dilute solution will not cause flocculation (e.g. curve 1 changed to 4), while a larger increase will (e.g. curve 1 changed to 6). The electrolyte content of sea water (approximately 36 g. salt per liter, of which about 24 g. [or .4 molar] is NaCl) is greater than that of curve 6.

F. Other Electrochemical Characteristics of Soil Colloids

There are other electrochemical characteristics of soil colloids which are important to the complete understanding of soil behavior. For example, zeta potential, which is the difference in potential between the "immobile" water layer and the bulk of the soil water, enters into such phenomena as electroosmosis. These other characteristics are not of direct enough importance to soil structure to warrant a consideration in this summary treatment.

XI. SOIL WATER

Since water plays an important role in interparticle forces, the nature of water in the soil will be considered next. Fig. 14a shows two soil particles with water between them; Fig. 14b shows a plot of the attractive force between the water and the particles versus the distance from them. The soil water can be divided into adsorbed water, which is attracted by forces from the soil strong enough to influence its behavior, and pore water, which is essentially free of soil attractive forces.

The attractive forces between the soil and adsorbed water are polar bonds, as illustrated in Fig. 15, and soil-water forces via the exchangeable cations. As has been discussed in Section X, the diffuse double layer on a colloid contains counterions which are hydrated. Since the counterions are attracted to the soil surface, the water of hydration they carry is in effect attracted by the soil.

As the absorbed water is under the influence of soil attractive forces, its behavior is different from that of the pore water. The part of the adsorbed water immediately adjacent to the soil is held by forces that are so strong that the water is immobile to normal hydrodynamic forces. The density, freezing point and other properties of this tightly bound water are different from those of liquid water. It can be considered as bound water which is part of the effective soil particle.

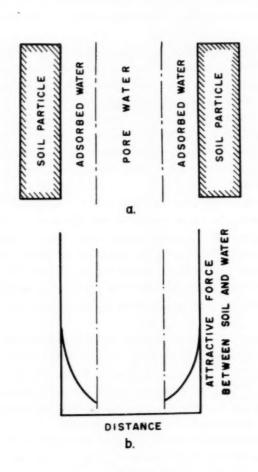
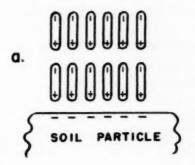


FIG. 14

The outer portion of the adsorbed water is partially immobilized and can be comsidered as viscous water. The forces between this water and the soil are of the same nature as those of the inner layer, but are weaker.

Many subdivisions of the adsorbed water have been suggested. The subdivisions have been based on arbitrarily selected points on the soil adsorption isotherm (plot of adsorbed water vs. pressure for constant temperature), or on the freezing temperaturewater content curve. The ADSORBED WATER



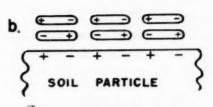


FIG. 15

Stern layer and the water layer at the point where the zeta potential is measured have also been used to classify the water in a soil system.

A subdivision (Michaels, 1952) of the adsorbed water that has merit considers the tightly bound water as "adsorbed" water and the partially immobilized water as "solvation" water. This tightly bound water is up to 10 molecules thick and is that water a dry soil would pick up in a humid atmosphere. The solvation water on a clay layer is from 20 to 200 molecules thick and is that additional water the clay, with its adsorbed water, would immobilize in a liquid environment.

The water in a soil system that is not under significant forces of attraction from the soil particle is pore water. Pore water follows hydrodynamic laws and, in general, behaves as normal liquid water. Essentially all of the water in a sandy soil is pore water; less than half the water in a saturated cohesive soil may be pore or free water.

One should realize that there is no fixed boundary between the various types of water. Just as the plot of potential versus distance

(Fig. 9) depended on several system variables, notably ion valence and concentration, the curve in Fig. 14 can be altered. In fact, one of the most promising approaches in the alteration of soil behavior with trace chemicals lies in the alteration of the thickness of immobilized water on a soil particle. In view of the fact that the thickness of the water layer is not a definite soil property, but varies with exchangeable ion, ion concentration, and water content (and probably other things), an entirely satisfactory subdivision can hardly be expected.

Some numerical data on adsorbed water will be helpful. The immobilized water on kaolinite as determined under various boundary conditions is:

Equilibrium water content at 50% relative humidity = 0.6 to 1.1%

Water immobilized during permeability test = $\mu_*6\%$ Equilibrium water content at a relative humidity a little less than 100% = 13 + %

Liquid limit = 38 to 55%

The amount of water which a soil will adsorb at 50% relative humidity is a good indication of the tightly bound water. There are also practical reasons for selecting 50% - the adsorption isotherm is almost horizontal in this region and 50% is a typical room humidity. For these reasons this measure has been used (Cornell 1951, Lambe 1952). The adsorbed water on kaolinite at 50% relative humidity varies with exchangeable ion from 0.6 to 1.1%. The corresponding range for montmortillonite is from 8 to 18%.

By measuring the permeability of kaolinite with various fluids, Michaels and Lin (1953, M.I.T. 1952) computed that water equal to 4.6% of the kaolinite weight was effectively immobile. This water (100 Å thick on an effective surface area of 4.6 square meters per gram) could be considered as part of the soil particle as far as permeability is concerned.*

The amount of water which a soil will adsorb at a relative humidity

^{*} Michaels and Lin found that the fluid flow caused a streaming potential which resulted in a "backflow". This backflow reduced the permeability and therefore made the immobile water layer appear thicker. The 100 A water thickness is too large and should be considered an effective, not actual, layer.

just under 100% can be used to approximate the adsorbed water. This is not a conveniently determined amount because the adsorption isotherm is almost vertical in the neighborhood of 100% relative humidity.

Since the liquid limit is the water content at essentially zero strength, it approximates an upper limit* of immobilized water. For kaolinite the liquid limit varies from 38% to 55%, depending on the exchangeable ion. The corresponding range for montmorillonite is much larger - 140 for iron to 710 for sodium.

One could, therefore, justifiably state the adsorbed water on kaolinite as anywhere from 0.6 to 55%, or on montmorillonite from 8 to 710%. While this vague meaning of "adsorbed" is certainly undesirable, no reforms are suggested at this time. Additional understanding of soil water may permit an intelligent and useful classification of soil water. This paper employs only the terms "adsorbed water" and "pore water" to describe soil water.

The preceding descriptions of water adsorption postulate that there is some order or orientation to the water molecules in the adsorbed layer. The degree of orientation varies with time and the discussion presented considers a statistical everage; this average amount of orientation is, of course, inversely related to temperature. There has been much theorizing on the orientation or structure of soil water, especially the adsorbed water; this theory is too idealized to warrant discussion here. The fact that the structure of soil water is unknown does not detract from this soil structure theory.

XII. INTERPARTICLE FORCES IN A SOIL MASS

We have considered at length the forces acting between particles which are some significant distance apart. The particles in an in situ soil deposit are not, however, far apart but are relatively close, even in the most porous soils. In sedimentary clays, the particles most likely formed flocs before settling out of suspension. The distances between particles in a soil mass are further decreased by the weight of soil

^{*} The maximum amount of adsorbed water on a soil would be present when the soil particles were in a dilute suspension. For example, in a hydrometer test where 50 grams of soil are dispersed in a liter of suspension, the adsorbed water on kaolinite is probably in excess of 100%, Not only does the liquid limit indicate the amount of adsorbed water, but also the interparticle attraction.

deposited on top of that being considered; they can also be decreased by the capillary forces from drying, by seepage forces, by the weight of glaciers and by man-placed loads. We shall, therefore, consider further possible interparticle forces to include those effective for small interparticle spacings. Attractive forces are first considered, then repulsive ones.

A. Attraction

1. van der Waals-London

This attractive force has been discussed in detail in connection with soil particles suspended in water. This force, of course, exists no matter how close the particles are together, and, in fact, gets much stronger as the particles approach (see Fig. 12). This is the universal attractive force and may be the only one effective in some soils.

2. Hydrogen Bond

Just as the hydrogen bond can be effective between oxygen and hydroxyl groups within a particle, it can act between discrete particles. For example, in kaolinitic soil, the particles may come together as Fig. 16 shows and permit a hydrogen bonding between the silica of one particle and the gibbsite of another. This is one of the strongest possible interparticle bonds.

3. Cations

Since essentially all soil particles are charged negatively, they attract cations to neutralize them, as has been discussed. An exchangeable cation attracted to two adjacent particles can act as a bridge between them, as illustrated in Fig. 17.

HYDROGEN BOND

CATION LINKAGE

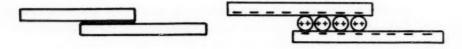


FIG. 16

FIG. 17

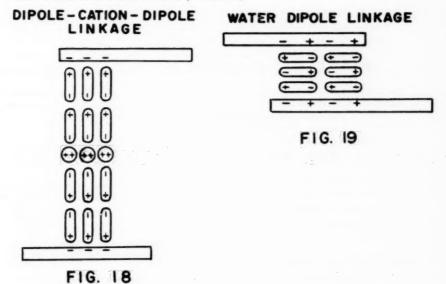
This cation linkage is similar to the intersheet bonds of illite, although much weaker because of lower negativity of the particle surface.

4. Dipole-Cation-Dirole

Farticles can be linked together through the water-cation-water mechanism illustrated by Fig. 18. This linkage would be a weak one, but could exist at relatively large distances.

5. Water Dipole Linkage

A dipolar linkage by water as illustrated by Fig. 19 is a possible attractive force between particles.



6. Ionic Rond

It is possible for two particles to bond ionically to each other just as the atoms in a crystal bond. For example, the edges of two kaolinite crystals (see Fig. 6) can be joined by the cations (aluminum and silicon) of one particle joining with the oxygens of the other particle. This type of joining amounts to crystal growth.

While soil particles probably bond to some extent by ionic bonds, such phenomena as sensitivity, thixotropy, and cohesion caused by consolidation suggest this type of bonding plays a negligible role in natural soils.

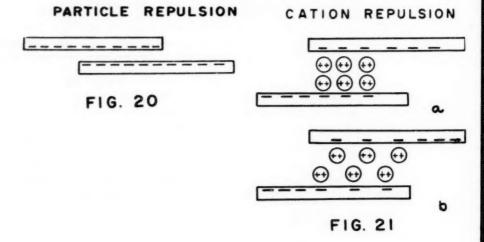
B. Repulsion

1. Particle Charge

Since the particles are similarly charged, they repel each other,

as shown in Fig. 20 and discussed in detail in Section X.
2. Cations

When two particles with exchangeable cations are brought close to each other, the cations tend to repel each other, since they carry like charges. This mechanism, represented in Fig. 21a, does not constitute a strong repulsive force between particles, since the mobile cations will move along the particle surface to positions not opposite other cations, as shown in Fig. 21b. The cation charge may also be entirely balanced by the particle charge, so that there is no cation-cation repulsion.



C. Summation of Forces

In the preceding pages, a number of possible mechanisms for attractive and repulsive forces between particles have been presented. The attractive and repulsive forces discussed in Section X exist even for particles which are actually touching, although the expressions of van der Waals forces do not hold, since the integrations cannot be correctly performed for extremely small distances. Additional forces can come into play when the particles are as close as those in the average natural soil. One can only speculate on which of the possible ones described are effective in any given soil. Additional information on these close-range forces is needed. Theoretical considerations do show that, for particles fairly close, the more closely they approach

each other, the stronger is the attractive internarticle force. Certainly the van der Waals-London forces are present; with distances smaller than about 10 angstroms these forces become very strong, and may be the only attractive forces that need be considered in many soil systems.

XIII. FORMATION OF A SEDIMENTARY CLAY DEFOSIT

Water, ice, wind, and gravity move the products of rock weathering until environmental conditions cause them to deposit these products as sediments. When streams flow into lakes, oceans or other bodies of relatively still water, they dump their transported load, since their load carrying ability is directly related to their velocity. Sedimentation of the colloidal load can be further aided, as in the case of marine deposits, by an increase of electrolyte concentration in the suspending medium.

When a river carries its load to a salt water body, the increase of electrolyte content usually causes flocculation of the colloids. While there should be some orientation of the flocculated clay particles, irrepresentations in electrical charge distribution, particles sterrically interfering with each other, and the forming of flocs large enough to be significantly affected by gravity make the orientation of particles in a marine clay very low (see Fig. 23). A result of this low degree of orientation is a highly porcus structure.

A fresh water dejosit, on the other hand, has a much higher degree of particle crientation (within small portions), and higher density, because the lack of electrical attraction between particles permits these colloids to seek positions of minimum energy.

The effect of electrolytes on sediment structure is in line with our colloidal theory, as evidenced by Fig. 13. It is also an experimental fact, as commonly demonstrated to students in soil courses by showing that a suspension of clay suddenly forms a curdled, loose sediment following the addition of a strong electrolyte solution, while a dispersed clay suspension slowly forms a dense sediment.

In summary, there is good documentation of principles employed in the above described process of clay formation.

XIV. CONSCLIDATION

As a sedimentary deposit increases in thickness, the overburden pressure at every depth increases. The additional pressure is initially

carried by the pore water as hydrostatic excess pressure. As the pore water drains because of the excess pressure, the additional pressure is transferred to the soil, which consolidates a volume equal to the volume of drained water. Other phenomena such as desiccation, seepage forces, glacier action and man-placed loads subject the clay deposit to consolidating pressures. During consolidation the particles come closer to each other, with the result that the interparticle forces increase - i.e., cohesion increases.

Even after the excess hydrostatic pressures in the pore water are dissipated, the particles continue to approach each other. During this very slow process the adsorbed water is extruded from between the particles and, to some extent, becomes pore water. While this process can occur with negligible volume change, other phenomena which contribute to secondary compression entail volume change. These other phenomena are the shifting of particles and the breakdown of aggregates. The higher the degree of particle order, the denser the soil and, therefore, the less the particle shifting and aggregate breakdown. In other words, a remolded soil with its higher order of particle orientation should have less of this contribution to secondary compression.

As two soil particles approach each other, their exchangeable cations repulse each other. When this repulsion exceeds the attraction of the soil for the ion, the ion may be forced from between the particles; it would take its hydration water with it. This ion expulsion occurs little, if at all, because of the increased rejulsion of particles resulting from counterion removal. Some of the hydration water on the ions is, however, squeezed out; some of the water adsorbed on the soil surface is also forced out. The extrusion, or diffusion, of adsorbed water can require many years to be completed. The transfer of adsorbed to pore water results in a strength increase, since the particles are closer together at points of contact, and in a permeability increase, since the volume of flow ghannels tends to increase.

^{*} Day and Holmgren (1952) have shown with photomicrographs the movement and breakdown of soil aggregates during compression.

^{**} The primary compression for the test on undisturbed Boston blue clay shown in Fig. 24 ranged from .45 to .67 of the total compression, while the corresponding range for the remolded test was .90 to .96.

As Fig. 13 illustrates, when particles are close together, any reduction of particle spacing results in an increase of attractive force. Since the slope of the potential curve is very steep at small distances, significant increases in cohesion result from minute decreases in particle spacing. The water between particles which are of the order of 10 A apart is not pore water, but water whose behavior is strongly influenced by force fields from the soil. The expulsion of this water must be done by forces large enough to overcome the attraction between the water and the soil, and also large enough to overcome steric deterrents to closer particle spacing. In other words, while the particles want to get closer, movement is a process req iring considerable time and applied force. The fact that this expulsion is accelerated by an increase in temperature accounts for the fact that more secondary compression is usually indicated by labcratery tests than occurs in situ. The laboratory soil is normally considerably warmer than the soil in situ.

Scils which have been subjected to high pressures for thousands of years have particles which are of the order of 3 Å apart at points of certact. The question of whether clay particles in natural deposits ever touch is really academic. The particle surfaces are not smooth, but are bumpy, to the extent of an angstrom. At points of centact, soil particles can "touch" as much as the border ions in a mineral crystal. Extreme amounts of time and pressure are required to get particles to spacings of less than 3 Å; steric deterrents and lattice interference minimize the points available for atom to atom centact.

Since our theory attributes part of secondary compression to the scil-liquid attractive forces, we can obtain useful data from consolidation tests on systems with different magnitudes of soil-liquid force. The soil-liquid linkage is a polar type of force and the dielectric constant ($\boldsymbol{\xi}$) of a liquid indicates its polarity; therefore, water ($\boldsymbol{\xi}$ = 81) and benzene ($\boldsymbol{\xi}$ = 2) were selected for soil liquids. Fig. 22 presents the results of a consolidation test on kaclinite with each liquid.

^{*} This observation has meen made many times by the Royal Swedish Geotechnical Institute, according to its director, Mr. Kjellman.

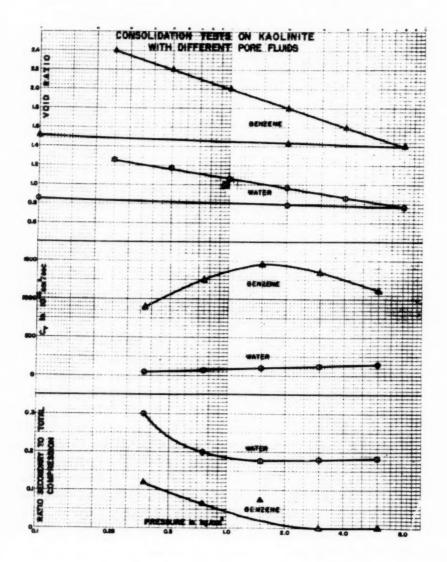


FIG. 22

These results show:

- 1. The ratio of secondary compression to total compression varied from 0.3 to 0.2 for water and from 0.1 to 0 for benzene. These are in the order predicted in our theory.
- 2. The ratios of total rebound to total compression were $\frac{0.091}{0.908}$ = .100 for water and $\frac{0.11}{2.79}$ = .039 for benzene. This order is in accord with our theory, since some of the adsorbed liquid squeezed out during secondary compression will return upon release of the pressure.
- 3. The coefficients of consolidation were 50 to 150 for water and 890 to 1460 for benzene. While void ratio and slope of void ratio versus pressure curve contribute to the difference in rate of consolidation, the biggest factor is permeability. The rate with which a liquid will flow through a bed of solids is, as our theory indicates, related inversely to the amount of liquid immobilized. The work of Lin and Michaels (1953) shows that kaolinite at a void ratio of 1.77 had a permeability to water of 3.5 x 10⁻⁶ cm/sec., and to benzene of 9.7 x 10⁻⁶ cm/sec.

Our theory indicates that the strength of a clay depends or the time under load, as well as the magnitude of load and the void ratio. The effect of time should be more important with a freshly deposited or a remolded clay than with an undisturbed one which has already had some of its adsorbed water squeezed from between the contact surfaces. Drying brings particles together (discussed in Section XVIII) and, therefore, can accomplish in a short time what extremely large pressures and long time do on a wet soil.

XV. LEACHING

During its long life, the natural soil is subjected to the flow of ground water. This ground water can deposit carbonates, sulphates, hydroxides, oxides, etc. which cement particles together at their points of contact. While the deposition of such substances is undoubtedly extensive, its contribution to the structure of the plastic soils is relatively minor.

An important action of the moving ground water is to alter the ionic concentration of soil water. The water in a soil deposited in a marine environment would almost always have ions removed by the leaching out of salt. This fact is evidenced by the many marine clays whose

pore water contains only a fraction of the salt in sea water. A typical marine clay would probably have the salt content of its water reduced from the 36 grams per liter of sea water to less than 5 grams per liter by thousands of years of leaching by relatively salt-free ground water.*

Since the adsorbed water is in equilibrium with the pore water, the counterions in the diffuse layers facing continuous pores - i.e., the accessible ions - are reduced in concentration. A reduction of ion concentration in the diffuse double layer results in an increase in the thickness of the diffuse double layer, as has been discussed. The ions which are not accessible to flowing water are less likely to be affected by the ion concentration alteration. There are undoubtedly many pockets or dead zones in the clay mass which are unaffected by leaching.

XVI. REMOLDING

Nearly all sedimentary clays lose strength when worked or remolded. The magnitude of this loss is indicated by "sensitivity", which is defined as the strength of the soil tested in an undisturbed state divided by the strength of the same sample tested after it has been thoroughly remolded.**

The remolding process can be reasoned from the preceding theory. Remolding pushes particles apart at points of contact and destroys some of the inaccessible or dead zones in the soil, thereby making the pore water in the system more nearly continuous. Separating the particles at points of contact causes a reduction in interparticle attractive forces (see Fig. 12), or cohesion. This process also increases the effective surface area of the soil particles and thereby the amount of adsorbed water in the system tends to be increased. In other words, the previously inaccessible particle surfaces now adsorb pore water.

^{*} An exchange of soil ions with ions brought in by ground water may have an effect on soil structure, as the data in Table 2 dramatically indicate.

^{**} Skempton and Northey (1952) and Rosenqvist (1953) have proposed an 8-step sensitivity scale running from "insensitive clays" having a sensitivity of 1 to "extra quick clays" having a sensitivity of >64.

There is one factor - particularly in the marine clays - which tends to reduce the increase of adsorbed water due to remolding. Releasing inaccessible counterions by remolding tends to increase the ionic concentration of the pore water. As has been discussed in detail, this increase of ion concentration results in a decrease of double layer thickness and, therefore, adsorbed water. Because the effect of the ion concentration changes is outweighed by the increase in effective surface area, remolding increases the adsorbed water in a clay.

Campbell (1952) has presented data on three soils which convincingly show more adsorbed water in each soil after remolding. One set of Campbell's data consists of plots of water content versus moisture suction. These curves indicate, for example, the following water contents at a suction of 1 atmosphere.

Soil	Unpuddled *(Undisturbed)	Puddled (Remolded)	
Chino clay loam	32%	36%	
Ft. Collins loam	16%	24%	
Pachappa fine sandy	10%	14%	
loam			

Campbell also shows that for any moisture content, the freezing point of the soil-water is less for the remolded soil. The author feels that Campbell's data furnish strong support to the theory that a soil has more adsorbed water when remolded than it did before remolding.

Remolding breaks, to some extent, the interparticle contacts and permits individual particles, on equal bases, to secure positions of minimum energy. Remolding, therefore, in effect, imparts an increased order to the arrangement of particles. It also destroys the largest voids that existed in the undisturbed soil. Remolding an undisturbed clay, therefore, does three important things:

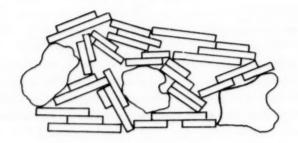
- 1. Increases the amount of adsorbed water at the expense of the pore water
- Increases the order of particle orientation within small portions of the soil.
- 3. Destroys the largest voids.

These changes are illustrated in Fig. 23.

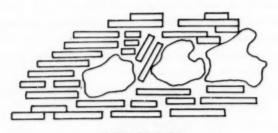
^{*} Campbell's "puddled" corresponds essentially to "remolded".



Salt Water Deposit



UNDISTURBED Fresh Water Deposit



REMOLDED

There are several important differences in the behavior of undisturbed and remolded clay which will now be examined in the light of our theory. The most apparent difference, that of higher strength for the undisturbed form, logically follows from the higher ion concentration at points of contact in the undisturbed (for marine clays) and the smaller interparticle distance at points of contact. The higher ion concentration results from a higher salt concentration in the water of a marine clay when formed than in the water of this clay after leaching. The closer interparticle spacing has been reached by subjecting the undisturbed clay to high loads for many years (or by drying). The importance of time for the expulsion of adsorbed water has been emphasized. The relationship between strength and structure is further discussed later.

In all cases reported, the permeability of a clay undisturbed is greater than that of the clay remolded. For example, the permeability of undisturbed Boston blue clay is about 200 times that of the same sample after remolding. This lowered permeability can be explained by the reduced amount of pore water - i.e., flow channels - by the higher degree of particle orientation, and by the destruction of the largest pores. or flow channels.

The higher frost heave for an undisturbed clay when tested in an open system (see Table I) than for the remolded sample can be explained in the same way that the permeability difference was.

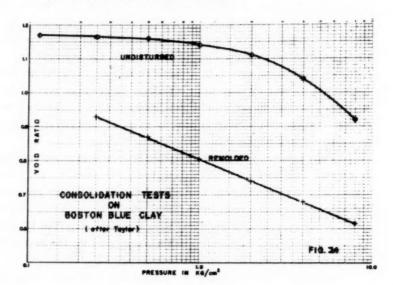
So11	TABLE	I	Per Cent Undisturbed	Heave Remolded
Boston blue clay Searsport clay			111.8 240.3	58.9 47.2

Fig. 24 (Taylor, 1942), which shows the consolidation curves for a Boston blue clay in the undisturbed and remolded states, illustrates two facts:

^{*} It is theoretically possible for a soil to have a higher strength when remolded than when undisturbed. For example, a recent fresh water deposit which had been subjected to only small pressure could gain strength by remolding. An increase of ion concentration in pore fluid would increase the chances for strength gain.

^{** &}quot;Frost Investigations, Fiscal Year 1951", Frost Effects Laboratory, Corps of Engineers, New England Division, Boston, Mass., June 1951.

- The curve for the remolded state is lower than that for the undisturbed state.
- The curve for the remolded is flatter than the virgin part of the curve for the undisturbed.



The higher degree of particle orientation and lower interparticle attraction in the remolded sample makes it much easier to obtain higher density with a given pressure; therefore, it is logical that the remolded curve is lower than the undisturbed curve. Since at any given consolidation pressure the remolded sample is denser than the undisturbed, it is reasonable that an increment of pressure will cause less densification in the remolded sample than in the undisturbed for pressures greater than the precompression load.

Another evidence of the higher density that can be obtained in a remolded soil is furnished by the void ratios of dry specimens. In

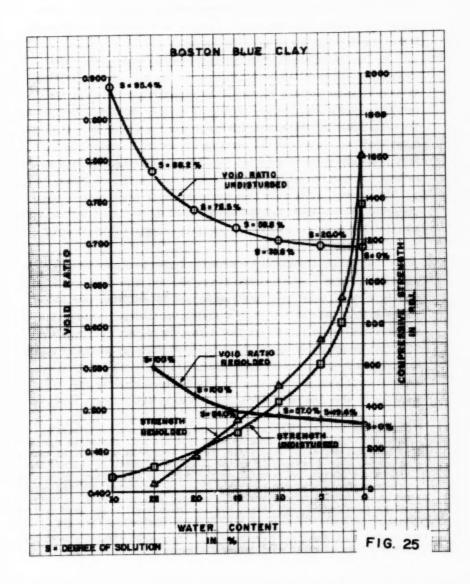


Fig. 25* is plotted the void ratio versus water content for an undisturbed sample and a remolded sample of Boston blue clay as they are dried. At any given water content, the remolded specimen is denser and at zero water content is $\frac{.690}{.1680}$ or 1.44 times denser. This higher dry density for the remolded sample is to be expected from the higher degree of order in the remolded soil.

In Fig. 25 is also plotted strength versus water content for undisturbed and remolded Boston blue clay. On this clay, remolding at natural water content decreases the strength and increases the particle orientation, thereby permitting greater density. Upon drying, the better particle orientation becomes more important, from strength considerations, than does the breaking of particle contact points. It is, therefore, to be expected that the remolded soil becomes stronger than the undisturbed at low water contents, as Fig. 25 shows.

In summary, it is felt that the known differences between undisturbed and remolded clay can be explained by our theory of structure. Additional data on soil water and particle orientation are needed. XVII. THIXOTROPY

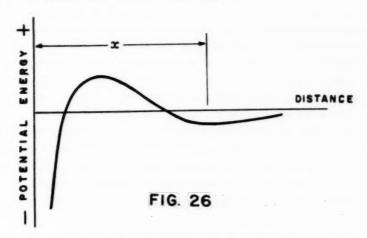
Thixotropy ("changing by touch") is the phenomenon of decreased viscosity with increased rate of shear exhibited by certain systems, such as dilute suspensions of sodium montmorillonite in water. When at rest such a suspension is a gel; when it is shaken it becomes a relatively low-viscosity liquid.

Thixotropy can be explained by means of plots of potential energy versus distance; such as is discussed in Section X. A colloidal suspension of such constitution that it is represented by Fig. 26 would exist with its particles x apart when at rest. Since this

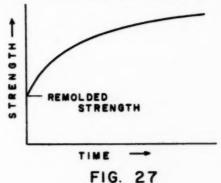
^{*} The curves in Fig. 25 point out another significant fact; namely, the simplified picture commonly held that all soil shrinkage occurs at constant degree of saturation, is not true. It was thought that a saturated clay decreased in volume upon drying until it reached its "shrinkage limit", below which drying occurred at constant volume. The author suggests that the shrinkage limit be abandoned, and the void ratio, or density of the dry soil, be used as a measure of minimum volume from drying. At least, the shrinkage limit needs more careful interpretation. The data in Fig. 25 were obtained by Lawrence (1951).

^{**} A system that shows the reverse - i.e., increased viscosity with increased rate of shear - is termed "dilatent".

shallow minimum state of energy is one of net attractive forces between particles, the system is a gel. Agitation furnishes enough energy to push the particles closer together where they repulse each other. The system then behaves as a liquid.



The term thixotropy is also used to describe the strength regain of a remolded soil. While one may question the selection of thixotropy to mean strength regain in a soil, he is faced with its wide use in this sense. Several experimentors have studied the rate at which a remolded clay regains strength; the results of these studies show a characteristic curve like Fig. 27. While a few of the tested soils regained 100% or more of the undisturbed strength, most did not.



* A summary and interesting discussion of strength regain data have been presented by Skempton and Northey (1952).

Since the environmental conditions during the forming and aging of a natural undisturbed clay, and during the remolding and storing of the remolded specimens are quite different, a strength-time plot for the original deposit should be unlike that of the remolded soil. The importance of the thousands of years of confining pressure to which the in situ deposit has been subjected has already been emphasized. The difference in ionic concentrations has also been discussed. The difference in particle orientation between the undisturbed and remolded clay has been pointed out.

Three of these differences (time, pressure and ionic concentration) would normally result in the remolded clay reaching a strength less than the undisturbed value. The better particle orientation in the remolded clay would tend to give the remolded sample higher strength. In general, the first three will outweigh the last and result in the remolded clay never (in reasonable lengths of time) regaining its undisturbed strength.

XVIII. DRY STRENGTH

A piece of dry clay may possess considerable strength. The forces that act between soil particles in a dry clay mass are ones which were effective in the wet clay, except, of course, those employing water. As a saturated clay mass dries it decreases in volume at such a rate that the volume-water content is initially a straight line (see Fig. 25). At some point the curve becomes increasingly flat. For desiccation above this point, the clay shrinks an amount equal to the volume of water which leaves the mass. The water is in tension because menisci are formed on the surface of the mass; a compression equal to the water tension is applied to the soil particles and causes a compression.

At degrees of saturation less than 100%, capillary pressures are still effective in isolated spots. As drying is continued further adscribed water is removed; this removal results in the interparticle distance being further decreased. As has been discussed at length, the shape of the potential-distance curve is such that at small distances a very small decrease in particle spacing is accompanied by a sharp increase in strength (see Figs. 13 and 25). One can understand, therefore, why a clay has such a high dry strength.

There are several possible mechanisms whereby the removal of adsorbed water reduces particle spacing. Among them are:

- Removal of water from either linkage described in Section XII A 4 or Section XII A 5 shortens the linkages and brings the particles together.
- Capillary pressures can be effective in an aggregate, or even between two particles, just as they were for the whole clay mass.
- 3. The replacement of water between particles by air, whose dielectric constant is less, results in a collapse of the double layer, i.e., a more rapid dissipation of the interparticle repulsion.

While the relative contribution of each cannot be definitely assessed, the water-soil polar bond certainly plays an essential part in the process. This fact is illustrated by the following data on the specimens which were dried at the end of the consolidation tests in Fig. 22.

Fig. 22.	Void Ratio in	Strength in Dry
System	Dry State	State
Benzene-kaolinite	1.32	zero
Water-kaclinite	0.71	Considerably greater than the sample with benzene

XIX. AGGREGATION AND DISPERSION

This paper has dealt at length with the forces acting between the various units of a soil mass, and has shown that these forces are electrochemical in nature. We will now briefly consider the alteration of these electrochemical forces by chemical additives, because such a consideration helps substantiate our theory of soil structure and gives us further insight into soil behavior.

There are chemicals which can greatly increase the interparticle forces in a fluid clay-water system and thereby cause the system to aggregate; similarly, there are chemicals which decrease interparticle forces or disperse the soil. Michaels (1952) has described in detail the various mechanisms by which aggregants and dispersants can act.

Sodium tetraphosphate, $Na_6P_{\downarrow}O_{13}$, is a very effective dispersant for soil systems. The polyphosphate can employ either one or both of two mechanisms to disperse the soil. The polyphosphate, by acting as a sequestering agent, can effectively remove the ions adsorbed on

the soil and replace them with sodium. This exchange increases the interparticle repulsion and therefore tends to disperse the soil. The phosphate polyanions can also bond to the soil particles through their exchangeable cations and the sodium ions attach themselves to the phosphate. Ultimately each soil particle will be surrounded by a polyanionic layer with its accompanying atmosphere of hydrated sodium ions. The hydrated sodium ions, in effect, push the particles apart because they increase the thickness of the diffuse double layer and therefore the adsorbed water layer. The experimental evidence (some adsorption of phosphate by soil, some phosphate not adsorbed) indicates that both mechanisms are employed.

One might think of the possible degree of structure of a soil system as existing between the limits of complete aggregation and complete dispersion. All natural clays when remolded exist between these limits, as evidenced by the fact that they can be further aggregated or further dispersed.

Soil aggregants and dispersants have considerable promise for use in soil stabilization, because of the pronounced effects they can have on the properties of soil in trace quantities. These effects have been discussed elsewhere (Lambe, 1952).

Since aggregants and dispersants alter soil properties by mechanisms which employ the same type of forces effective in natural soil, they can be used to examine our theory. Our theory leads us to believe that the leaching of an undisturbed clay with a dispersant will reduce to a limited extent the undisturbed strength and to a marked extent the remolded strength. Were it not for the inaccessible points of particle contact, the undisturbed strength could be made equal to zero. The data in Table 2 show our theoretical predictions are correct.

		LADL	2 6		
Soil		Leached With		Undisturbed Strength, psf	Remolded Strength,psf
Boston blue	clay	water	_	450	41
Boston blue		water + 0.5%	Na 6Ph 013	320	0
Boston blue	clay	water + 1.0%		220	0

* weight
$$Na_6P_4O_{13}$$
 = 0.5% soil dry weight
** weight $Na_6P_4O_{13}$ = 1.0% soil dry weight

TADIE A

A sample of dispersed soil should dry to a high density and obtain a high dry strength. Realizing that remolding partially disperses the soil, one would expect better particle alignment, and, therefore, higher dry density and higher strength from a chemically dispersed soil than from a remolded - i.e., mechanically dispersed-soil. The following data on a sample of Boston blue clay show this expectation to be a fact:

Remolded Boston blue clay dry strength 263 psi Na $_6$ P $_1$ O $_1$ 3

XX. SUMMARY AND CONCLUSIONS

This paper presents a detailed theory to explain the structure and behavior of fine grained soil. The forces which act between bodies are first described and them employed to build up successively the units of a natural soil. Next the electrokinetic behavior of soil particles is treated in terms of the principles of colloidal chemistry. The presented theory is used to explain such soil phenomena as structure, remolding, consolidation, cohesion, dry strength, secondary compression and strength regain.

This theory of structure has many facets which need expansion and probably parts which need correction. It should serve as a working guide which extensive and ingenious experiments will improve.

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